Measured Concentrations of Herbicides and Model Predictions of Atrazine Fate in the Patuxent River Estuary

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ABSTRACT

The environmental fate of herbicides in estuaries is poorly understood. Estuarine physical transport processes and the episodic nature of herbicide release into surface waters complicate interpretation of water concentration measurements and allocation of sources. Water concentrations of herbicides and two triazine degradation products (CIAT [6-amino-2-chloro-4-isopropylamino-*s*-triazine] and CEAT [6-amino-2-chloro-4-ethylamino-*s*-triazine]) were measured in surface water from four sites on 40 d from 4 Apr. through 29 July 1996 in the Patuxent River estuary, part of the Chesapeake Bay system. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was most persistent and present in the highest concentrations (maximum = 1.29 μg/L). Metolachlor [2-chloro-6′-ethyl-*N*-(2-methoxy-1-methylethyl)-*o*-acetoluidide], CIAT, CEAT, and simazine (1-chloro-3,5-bisethylamino-2,4,6-triazine) were frequently detected with maximum concentration values of 0.61, 1.1, 0.76, and 0.49 μg/L, respectively. A physical transport model was used to interpret atrazine concentrations in the context of estuarine water transport, giving estimates of in situ degradation rates and total transport. The estimated half-life of atrazine in the turbid, shallow upper estuary was $t_{1/2}$ = 20 d, but was much longer ($t_{1/2}$ = 100 d) in the deeper lower estuary. Although most (93%) atrazine entered the estuary upstream via the river, simulations suggested additional inputs directly to the lower estuary. The total atrazine load to the estuary from 5 April to 15 July was 71 kg with 48% loss by degradation and 31% exported to the Chesapeake Bay. Atrazine persistence in the estuary is directly related to river flows into the estuary. Low flows will increase atrazine residence time in the upper estuary and increase degradation losses.

The Chesapeake Bay system has important historical, cultural, and economic significance for the entire Mid-Atlantic region of the United States. It is a complex system of large and small tributaries woven through a five-state area with many different land use categories within its watershed. The system is threatened by a variety of point and nonpoint pollution sources. Agriculture remains a significant industry in the watershed, with corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] production being the dominant crops. Within the state of Maryland, 8 of the top 11 most used pesticides are herbicides, representing approximately 1.2×10^6 kg applied each year (Maryland Department of Agriculture, 1999). Previous studies have been conducted to determine loads of pesticides entering the Chesapeake Bay at the fall lines of major tributaries (Foster and Lippa, 1996; Godfrey et al., 1995; Foster et al., 2000; Liu et al., 2002); however, little is known regarding the fate of these chemicals in the tidal portion of the rivers. Herbicides have been found to harm the lower levels of the estuarine food chain either directly (Lytle and Lytle, 1998; Detenbeck et al., 1996; Fairchild et al., 1998; Pennington and Scott, 2001) or synergistically with other pesticides (DeLorenzo et al., 1999; Pape-Lindstrom and Lydy, 1997; Jin-Clark et al., 2002). Therefore, more information is needed to assess the concentrations and persistence of herbicides in the tidal portion of rivers in the Chesapeake Bay system.

The Patuxent River estuary is the largest river basin located completely in the state of Maryland. A detailed description of the watershed and agricultural activity in the area was published by Harman-Fetcho et al. (1999). The watershed is typical of many in the Chesapeake Bay region in that it contains a combination of agricultural, forest, and urban land uses. In the springs of 1994 and 1995, a preliminary study was performed to determine pesticide concentrations in the surface water of the lower Patuxent River and to compare these results with river flow and estimated pesticide use patterns (Harman-Fetcho et al., 1999). The herbicides atrazine, simazine, and the triazine breakdown product CIAT were consistently higher than the other pesticides included in the study and were found at the highest levels in the upper estuary. A significant finding from the study was that a large portion of the pesticide entering the Patuxent estuary appeared to originate above the upstream station and the maximum concentrations were found after rain events. However, most of the samples in the earlier study were collected at the mouth of the river and the number of samples collected from the upstream stations was small. From these results it was difficult to accurately assess the fate of these chemicals in the estuary. The goal of the current study was to frequently characterize the concentration of herbicides along the estuary salinity gradient such that the data could be used in an estuarine transport model to gain important insights into the behavior of atrazine and other persistent herbicides in estuaries of the Chesapeake Bay system. The model was used as a means to infer the location of major sources and to estimate the residence time and half-life of atrazine in the Patuxent River.

MATERIALS AND METHODS

Sample Collection, Processing, and Analysis

Surface water samples (1-L volume) were collected from four shore-based locations (Jug Bay, Benedict Bridge, Patterson Park, and Solomons) on the lower Patuxent River on 40 d between 4 Apr. and 29 July 1996 (Fig. 1, Table 1, site coordinates). River water was collected on 4, 8, 15, 22, 24, 26,

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29, and 30 April, every day from 1 May to 11 May, every other day from 13 May to 28 June, and on 1, 8, 15, 22, and 29 July. Three sampling cruises of the river were also performed that included six or seven sites on 15 April, 10 May, and 22 May (Fig. 1). Temperature, salinity, total suspended particle concentration, and dissolved organic carbon were measured for each sample (Table 1).

Surface water was obtained from shore-based sites using a solvent-rinsed aluminum bucket, which was used to fill a clean stainless steel can. Water was filtered on-site through a Whatman (Maidstone, UK) GF/F filter using a stainless steel filter holder. Filtered water was captured in a 1-L amber glass bottle with a Teflon-lined lid and placed on ice until processing and analysis. The remaining water (5–15 L) in the stainless steel can was transported to the USDA for filtering through a 142-mm GF/F filter to obtain particles for analysis of particle-phase pesticide concentrations.

Filtered water was also retained for dissolved organic carbon analysis, while unfiltered water was saved for total suspended particle measurements. Water for DOC analysis was filtered further using a 13-mm, 0.2-μm Teflon membrane syringe filter (Gelman Acrodisc CRPTFE; Gelman Sciences, Ann Arbor, MI) and was analyzed by the combustion–infrared method (USEPA, 1983). Total suspended particle concentration was determined by filtering 100 to 250 mL of water through a preweighed membrane filter (47-mm-diameter Nucleopore polycarbonate membrane filter, 0.4-μm pore size).

During the cruises, water samples were collected from the bow while the boat moved slowly upstream to avoid contamination from the motor. Samples were filtered at the end of the day in the laboratory. Temperature and salinity were measured using a YSI (Yellow Springs, OH) Model 33 meter at each station.

Dissolved-phase water samples were extracted within 5 d of collection in batches including a distilled water blank, a distilled water spike, and two river water spike samples. Each sample and control was spiked with 200 ng each of ^{13}C-labeled metolachlor and ^{13}C-labeled atrazine (Cambridge Isotopes, Andover, MA) before extraction to determine extraction efficiency. Spike samples were fortified with 200 to 600 ng each of target analytes before extraction to measure the overall efficiency of the method. Water samples were extracted using solid-phase extraction (SPE) cartridges containing 1 g of octadecyl phase (tC18 Waters Sep Pak; Waters Associates, Milford, MA). Before extraction, cartridges were preconditioned with 5 mL of methanol and 5 mL of distilled water; 5 mL of methanol was added to the water sample as recommended by the manufacturer for maximum performance of the solid phase. Water was pulled directly from the glass bottle through Teflon tubing to the SPE cartridge using a vacuum manifold at a flow rate of approximately 20 mL/min. The SPE cartridges were not allowed to become dry during extraction.

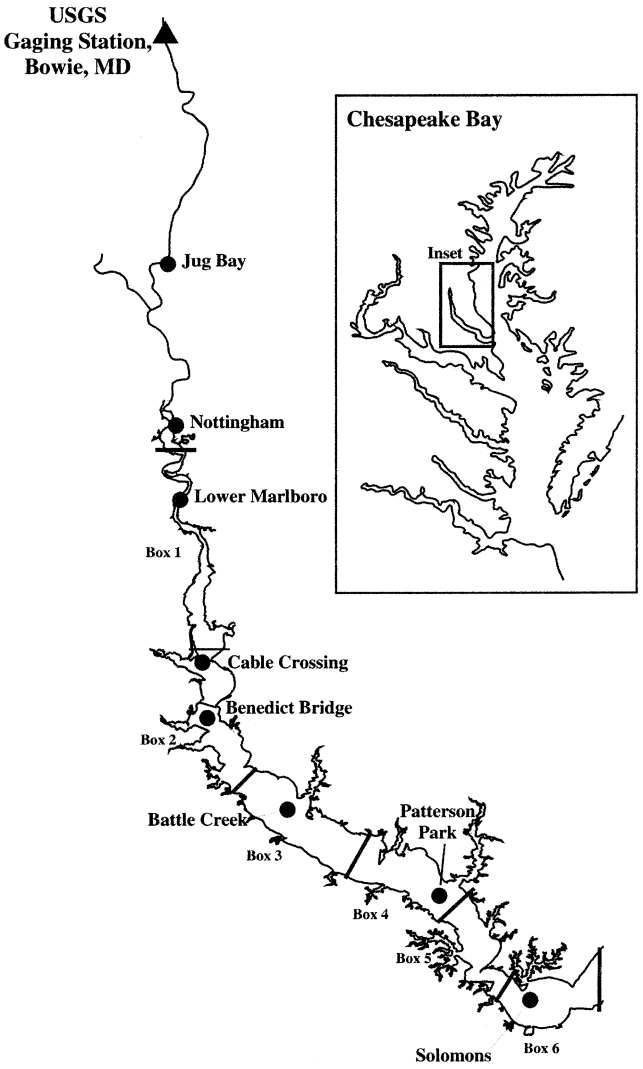

Fig. 1. The Chesapeake Bay and the Patuxent River with sample collection sites and box model segments.

After extraction, cartridges were air-dried for 10 to 15 min to partially remove residual water before elution. Cartridges were eluted with 3 mL each of ethyl acetate, ethyl acetate and dichloromethane (1:1), and dichloromethane (pesticide-grade solvent; Burdick and Jackson, Muskegon, MI). Anhydrous sodium sulfate was added to the eluent to remove any remaining water. Extracts were reduced to 0.5 mL under a gentle stream of high-purity nitrogen gas for analysis.

Samples were analyzed using capillary gas chromatogra-

Table 1. Sample collection locations used in this study and measured temperature, salinity, and total suspended particle concentration measurement results.

Site name	Coordinates	Salinity range	Temperature	TSS†	DOC‡
		g/L	°C	mg/L	μg C/L
Jug Bay§	38°48′ N, 76°43′ W	0–0.5	13–26	6.8–54	1.6–7.0
Nottingham	38°43′ N, 76°42′ W	0–2.5	14–25	13–49	3.8–5.9
Lower Marlboro	38°39′ N, 76°40′ W	0–2.5	13–24	26–58	3.9–4.7
Cable Crossing	38°35′ N, 76°40′ W	1.5–3.1	14–18	25–81	2.6–3.0
Benedict Bridge§	38°31′ N, 76°40′ W	3.0–8.9	15–29	11–200	1.4–11
Battle Creek	38°27′ N, 76°36′ W	7.0–7.2	17–21	3.9–6.2	4.1
Patterson Park§	38°23′ N, 76°32′ W	6.0–19	10–30	4.6–19	1.3–11
Solomons§	38°19′ N, 76°27′ W	6.0–12	11–27	3.0–8.8	1.9–13

† Range of total suspended particle concentrations in water over the study period.
‡ Range of dissolved organic carbon concentrations in water over the study period.
§ Shore-based sites. Remaining sites were only sampled during three cruises in April and May.

phy–mass spectrometry (GC–MS) with a Hewlett-Packard (Palo Alto, CA) 5890 GC coupled to a 5989A MS in electron impact mode and programmed for selected-ion-monitoring mode (Harman-Fetcho et al., 1999). Blank samples showed no interfering peaks. Recoveries were acceptable for all compounds except for the two triazine degradation products, CIAT and CEAT, which consistently averaged 22 to 25% recovery in river water (Table 2). Therefore, measured concentrations of CIAT and CEAT were adjusted using these recovery values to reflect the actual levels in the water. No other chemicals in the study were adjusted for their recovery values. Recoveries of the surrogate compounds, cyanazine, and metolachlor averaged >100%. This may indicate that the response of these compounds is higher in the presence of co-eluted material present in the extract as compared with clean solvent used to make calibration standards. A quantification limit of 0.023 μg/L was used for all analytes based on the range of calibration solutions used (10% below lowest calibration point). This quantification limit is well above the instrumental detection limit for our analytes.

A number of particle-phase filter samples (n = 57) were randomly selected for extraction and analysis to screen for particle-phase residues. Filter samples were extracted in batches including one blank filter and one blank filter spiked with a mixture of target analytes. Each sample was spiked with a surrogate compound, diazinon-d_{10}, to measure extraction efficiency. Filters were placed in a Soxhlet apparatus and extracted for at least 8 h using dichloromethane. The extract was reduced to 10 mL volume using rotary evaporation, passed through a clean-up column of 1 g of anhydrous sodium sulfate and 2 g of alumina (Supelclean LC-Alumina-N SPE tube, 6 mL; Supelco, Bellefonte, PA), and reduced to 1 mL for analysis by GC–MS in the same manner as dissolved-phase samples. This method has been proven to be efficient in extracting our target analytes (77–103% recovery) from water filter matrices with the exception of CIAT, which is recovered at an average of 38% (Liu et al., 2002). Blank samples showed no interfering peaks. Method detection limits ranged from 0.0003 to 0.0016 μg/L for our target analytes in a 10-L sample. None of the samples had levels above our quantification limits; therefore, only operationally defined dissolved-phase concentrations will be reported in the Results and Discussion.

Table 2. Analyte list, mean spike recovery results for distilled water and river water matrices, and estimated annual usage in the Patuxent River watershed.†

Compound name	Spike recovery		Estimated annual usage in watershed
	Distilled water (n = 10)	River water (n = 22)	
	%		kg
Acetochlor	63 ± 30	75 ± 27	14 000
Alachlor	83 ± 32	87 ± 14	4 100
Atrazine	65 ± 10	69 ± 18	21 000
Atrazine–^{13}C‡	136 ± 26	106 ± 31 (n = 198)	
CEAT§	9 ± 7	22 ± 11	
CIAT¶	12 ± 5	24 ± 15	
Cyanazine	53 ± 30	123 ± 92	1 700
Metolachlor	114 ± 45	111 ± 22	23 000
Metolachlor–^{13}C‡	130 ± 51	119 ± 26 (n = 198)	
Pendamethalin	40 ± 23	46 ± 5	36 000
Simazine	73 ± 24	70 ± 48	9 708

† Recovery values are listed as mean percent recovery ± standard deviation. Pesticide usage estimates were calculated from Maryland Department of Agriculture (1999) county-based data from 1997 multiplied by the fraction of the Patuxent River watershed area within that county.
‡ Surrogate chemical added to each sample and control before extraction.
§ Triazine degradation product (6-amino-2-chloro-4-ethylamino-*s*-triazine).
¶ Triazine degradation product (6-amino-2-chloro-4-isopropylamino-*s*-triazine).

Physical Transport Model Description

The estuarine water transport model is a salt and water balance box model (hereafter "box model") adapted from the model first proposed by Pritchard (1969) and further developed by Officer (1980) and Hagy et al. (2000). The model was directly adapted from the Patuxent River box model described by Hagy et al. (2000). Details of the data sources and computations can be found therein. A general summary is provided below.

The box model computed water transport by solving the system of linear equations representing conservation of water volume and salt mass within a series of estuarine segments. The box model includes six segments (Fig. 1). All but the most landward segment in the model were divided vertically at the pycnocline into surface and bottom layer boxes. All boxes were assumed to be well-mixed.

Consistent with field observations, the circulation of the estuary was assumed to be the classical two-layer estuarine circulation in which the residual circulation (i.e., remaining after subtracting tidal currents) is seaward in surface waters and landward in bottom waters (e.g., Pritchard, 1952). Water volume is conserved by continuous upwelling along the salinity gradient, while vertical salt continuity is maintained by vertical diffusive exchange at the pycnocline.

Freshwater inputs to each surface layer box were estimated as the sum of gauged runoff, ungauged runoff, and precipitation minus evaporation. Patuxent River is gauged near the fall line at Bowie, MD (Fig. 1). The gauged watershed area accounts for about 40% of the watershed area. Monthly precipitation and evaporation measurements were obtained from National Oceanic and Atmospheric Administration (NOAA) climatological summaries (National Oceanic and Atmospheric Administration, 1996) and applied to open water areas. Runoff from ungauged portions of the watershed was computed from the flow per watershed area in gauged areas with modifications according to the water budgeting procedure of Hagy et al. (2000). The water budget was validated by comparison with a hydrologic simulation model (Linker et al., 1999, as reported by Hagy et al., 2000).

Salinity distributions were obtained from the USEPA Chesapeake Bay Water Quality Monitoring Program (USEPA, 2002), which measured salinity throughout the water column at a series of nine stations down the axis of Patuxent River on a biweekly basis during the study period. Average salinity was computed for each box using a volume-weighting procedure that accounts the varying cross-sectional volume per meter depth and axial distance (Hagy et al., 2000).

The salinity regime and freshwater inputs changed during the study period. Therefore, it can be expected that the transport regime within the estuary changed as well. Because the model assumes complete mixing within model segments, short-term variations in the flow regime probably cannot be resolved. However, we sought to compute daily incremental changes in the transport regime consistent with the changes over monthly time scales. To obtain daily estimates, while ensuring conservation of water volume and salt mass each day, the salinity and freshwater input data were extrapolated to daily time series. A cubic spline was used to extrapolate to a daily interval (PROC EXPAND; SAS Institute, 1993) to avoid discontinuity in the derivative of salinity with respect to time, which would cause discontinuous and artifactual changes in the computed physical transport regime.

Simulation of Atrazine Concentration

The time series of estimated physical transport parameters was used to simulate changes in atrazine concentration in the

estuary under various assumed internal loss rates and various scenarios for down-estuary ("local" inputs) of pesticide. Initial values for the concentration of atrazine throughout the estuary were based on surface water samples collected during the transect cruise on 15 April. Initial bottom layer concentrations were assumed to be equal to surface layer concentrations. Fluvial input of atrazine was computed as the product of daily freshwater inflow and the daily atrazine concentration at Jug Bay (Fig. 1). Similarly, the input of atrazine at the seaward end of the estuary was computed as the product of daily inflow of seawater into the bottom layer of Box 5 and the daily concentration observed at Solomons. Where gaps were present in the daily record of atrazine concentration at Jug Bay and Solomons, these values were computed from adjacent time points by fitting a cubic spline (PROC EXPAND; SAS Institute, 1993).

At each time step in the simulation, the change in the atrazine concentration in surface layer boxes was computed as:

$$V_m \frac{dc_m}{dt} = Q_{m-1}c_{m-1} + Q_{vm}c'_m + E_{vm}(c'_m - c_m) + E_{m+1,m}(c_{m+1} - c_m) - E_{m,m-1}(c_m - c_{m-1}) - Q_m c_m - kV_m c_m \quad [1]$$

where V_m is the volume of the surface layer box in segment m; Q_{fm} is freshwater input to segment m; Q_m is seaward advection from box m into box $m + 1$; E_{vm} is the rate of vertical non-advective exchange (i.e., across the pycnocline) in segment m; $E_{m,n}$ is the rate of horizontal non-advective exchange from surface layer box m to surface layer box n; c_{fm} is the concentration of pesticide in freshwater entering segment m; c_m is the concentration of pesticide in surface layer box m; C'_m is the concentration of pesticide in the bottom layer box m; and k_m is the first-order pesticide decay coefficient applicable to segment m. The following also apply: when $m \neq 1$, $E_{m+1,m} = 0$; when $m \neq 2$, $E_{m,m-1} = 0$; when $m = 1$, $Q_{vm} = 0$ and $E_{vm} = 0$. When $m = 1$, Q_{m-1} is the river discharge at the upstream limit of Box 1 (i.e., Q_r) and c_{m-1} is the concentration at Jug Bay. The same equation for bottom layer boxes is:

$$V'_m \frac{dc'_m}{dt} = Q'_{m+1}c'_{m+1} - Q_{vm}c'_m - E_{vm}(c'_m - c_m) - Q'_m c'_m - k_m V'_m c'_m \quad [2]$$

where V'_m is the volume of the bottom layer box in segment m and Q'_m is landward advection in the bottom layer from segment m to segment $m - 1$. For $m = 5$, c'_{m+1} is the concentration at Solomons. Simulations were run using a time step (Δt) of 1 h and Euler integration, namely:

$$C(t + \Delta t) = C(t) + \frac{dC(t)}{dt}\Delta t \quad [3]$$

where $C(t)$ is the concentration in any box at time t. This was sufficient to reduce integration errors to negligible levels based on simulations run using shorter time steps (Jeffers, 1988).

First-order decay rates (k_m) and inputs of pesticide directly to the estuarine portions of the river (i.e., Q_{fm}, c_{fm}) were estimated by comparing observed values to model predictions obtained using a range of parameter values. Parameter values were selected that best reproduced mean values for the Benedict Bridge and Patterson Park sites. It was not expected that the model would predict the short-term fluctuations, which may reflect small-scale spatial and temporal variability not simulated by the model. Model predictions were not compared with values for Jug Bay and Solomons locations because these concentrations were used as the upstream and downstream boundary conditions for the simulations.

RESULTS AND DISCUSSION

Pesticide Use Patterns and Measured Concentrations

The Patuxent River watershed is held within the boundaries of five Maryland counties: Anne Arundel, Calvert, Howard, Montgomery, Prince George's, and St. Mary's. The dominant crops grown in these counties are corn, soybean, and tobacco (*Nicotiana tabacum* L.) (Harman-Fetcho et al., 1999). In the Mid-Atlantic region corn is planted in early May, soybean is planted in early to mid-June, and herbicides are normally used preemergence in both crops. Triazine herbicides such as atrazine and cyanazine are frequently used on corn (Meister, 2001). Acetanilide and chloroacetamide herbicides like metolachlor, alachlor, and acetochlor may be included in the formulations used at corn planting or they may be used on soybean. Pendamethalin and simazine are selective herbicides used on a variety of crops, turf, and ornamentals. Previous research in other Chesapeake Bay tributaries (Lehotay et al., 1999; Liu et al., 2002; Glotfelty et al., 1984) and in the Patuxent River (Harman-Fetcho et al., 1999) has shown that the highest herbicide concentrations are found in surface waters in May and June, coinciding with runoff events after corn and soybean planting.

County-based pesticide use data are available for 1997 (data from 1996 is not available) from the Maryland Department of Agriculture (1999). Using the fraction of the Patuxent River watershed in each county, an estimate of the herbicide usage in the watershed can be calculated (Table 2). Pendamethalin, metolachlor, and atrazine were used in the highest amounts: 36 000, 23 000, and 21 000 kg/yr, respectively. Use of acetochlor, estimated at 14 000 kg/yr, was only reported in Howard county in the northernmost region of the watershed. The remaining chemicals had an estimated use rate of $<$10 000 kg/yr.

Atrazine was present in the highest concentration of any of the target analytes (1.29 μg/L) and was the herbicide most frequently detected at all four stations (100, 97, 72, and 77% detection at Jug Bay, Benedict Bridge, Patterson Park, and Solomons, respectively) (Table 3). Atrazine has a long half-life in soil (60 d) (Montgomery, 1993) and freshwater (140 d) (Rice et al., 1997), and is observed year round in surface waters in the Midwest region of the United States (Schottler et al., 1994). Mean atrazine concentrations decreased from 0.28 to 0.036 μg/L from Jug Bay to Solomons, respectively, indicating an upstream atrazine source with dilution and/or degradation processes reducing concentrations as the water moves through the estuary. The two triazine degradation products included in this study, CEAT and CIAT (Fig. 2) (sometimes referred to in the literature as desisopropylatrazine [DIA] and desethylatrazine [DEA], respectively), were detected less frequently than atrazine, but maximum and mean concen-

Table 3. Concentration data for herbicides and their breakdown products in the Patuxent River from sample collection sites, April–July 1996.†

Parameter	Acetochlor	Alachlor	Atrazine	CEAT‡	CIAT§	Metolachlor	Simazine
	µg/L						
			Jug Bay (n = 40)				
Mean	0.055	0.122	0.28	0.43	0.26	0.15	0.135
Minimum	0.050	0.029	0.033	0.14	0.029	0.044	0.025
Maximum	0.060	0.54	1.29	1.1	0.76	0.61	0.49
Detection, %	5	25	100	45	80	100	75
			Benedict Bridge (n = 37)				
Mean	ND¶	0.038	0.1	0.3	0.13	0.05	0.058
Minimum		0.032	0.024	0.1	0.081	0.023	0.030
Maximum		0.044	0.36	0.52	0.19	0.26	0.15
Detection, %		5	97	35	24	92	43
			Patterson Park (n = 40)				
Mean	ND	ND	0.048	0.34	0.18	0.034	0.032
Minimum			0.027	0.12	0.18	0.024	0.029
Maximum			0.091	0.63	0.18	0.046	0.033
Detection, %			72	28	3	25	8
			Solomons (n = 39)				
Mean	ND	ND	0.036	0.49	0.17	0.037	0.042
Minimum			0.026	0.19	0.17	0.027	0.03
Maximum			0.084	0.87	0.17	0.053	0.065
Detection, %			77	31	3	18	8

† Cyanazine and pendamethalin were not detected above quantification limits in any samples. The quantification limit for all analytes was 23 ng/L. Mean values represent the average of all values above the limit of detection.
‡ Triazine degradation product (6-amino-2-chloro-4-ethylamino-*s*-triazine). Spike recoveries for this chemical in river water were 22 ± 11%, so reported concentrations have been adjusted for recovery values to more accurately reflect the real levels in the river.
§ Triazine degradation product (6-amino-2-chloro-4-isopropylamino-*s*-triazine). Spike recoveries for this chemical in river water were 24 ± 15%, so reported concentrations have been adjusted for recovery values to more accurately reflect the real levels in the river.
¶ Not detected.

tration values were often greater than atrazine, especially at the downstream sites (Table 3).

Metolachlor was also frequently detected at the two upstream locations (≥92%), but concentrations often fell below the analytical limits of detection at the downstream stations (18–25% detection). Metolachlor maximum and mean concentrations were generally lower than atrazine. Because usage of these two chemicals is similar within the watershed area (around 20 000 kg/yr), it appears that metolachlor is not as efficiently transported to surface waters nor as stable in an estuarine environment. Alachlor was only detected at the two upriver stations and acetochlor was only detected at Jug Bay in 5% of samples. The shorter persistence of these chemicals has also been observed by Aga and Thurman (2001), who found that metolachlor and alachlor had soil half-lives of only 15.5 and 8 d, respectively. In experiments in aquatic field mesocosms conducted by Graham et al. (1999), metolachlor and alachlor had half-lives of 33 to 46 and 18 to 21 d, respectively. The median

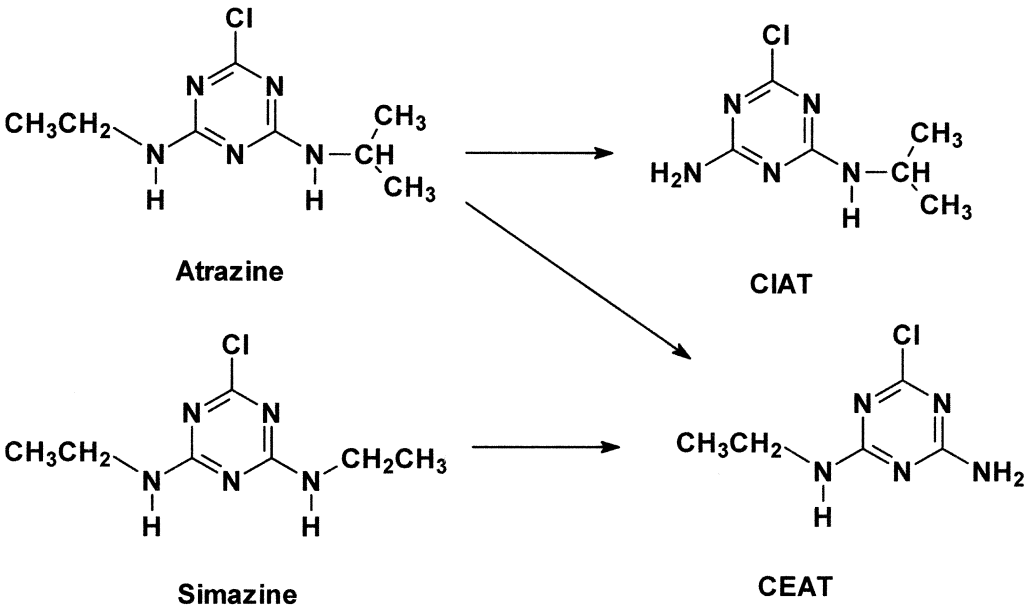

Fig. 2. Dealkylation products of atrazine and simazine: CIAT (6-amino-2-chloro-4-isopropylamino-*s*-triazine) and CEAT (6-amino-2-chloro-4-ethylamino-*s*-triazine). Other degradation products can be formed from atrazine and simazine.

residence time for freshwater entering Patuxent estuary entering near Jug Bay is 68 d (Hagy et al., 2000); thus, significant degradation of these chemicals in surface water would be expected before reaching the mouth of the river.

Simazine was also frequently detected at the two upper stations (≥43% detection) with mean concentrations somewhat lower than metolachlor at these upstream locations, but it was only detected in 8% of samples at Patterson Park and Solomons. Therefore, while these chemicals may be entering the river, they are not persistent in estuarine surface waters. Cyanazine and pendamethalin were not detected in any samples at levels above the limits of detection. Cyanazine was not used in large quantities in the Patuxent watershed at the time of this study (approximately 1700 kg/yr), and published soil half-life values (14 d) (Montgomery, 1993) for this chemical are lower than the other triazines. Pendamethalin was used in significant quantities at the time of this study (36 000 kg/yr), but it does not appear to move efficiently into surface waters in this watershed in the parent form.

Dissolved-phase concentration results in this study are similar to the study of the Patuxent River conducted in 1994 and 1995 by Harman-Fetcho et al. (1999) in that the highest herbicide concentrations were present at the upstream site, Jug Bay, and the lowest concentrations were found at Solomons, near the mouth of the estuary. A comparison of maximum concentrations reveals that higher levels of atrazine and simazine were present in 1995 (Table 4), but maximum alachlor and metolachlor levels were higher in 1996. These differences could be a result of changes in herbicide use patterns in the watershed or simply differences in weather conditions or the timing of sample collection between the two studies. Results presented in Table 4 from 1994 represent measurements from the Solomons station only. Concentration values are therefore lower overall than the two subsequent years.

An examination of temporal trends at the four stations reveals that herbicide concentrations at the Jug Bay station were highly variable with large, sharp, and concurrent peaks of all the herbicides (Fig. 3). Peaks in herbicide concentrations at the Benedict Bridge site were broader than at Jug Bay with the exception of one, sharp, multiherbicide peak occurring on June 19. The temporal patterns at the two downstream stations were less defined with a broad peak of metolachlor occurring at both stations around 11 to 14 May and a sharper peak of both atrazine and metolachlor on June 14. Atrazine concentrations at both lower stations after mid-May remain fairly constant through mid-July at approximately 0.060 μg/L at Patterson Park and approximately 0.040 μg/L at Solomons. These results suggest that the sharp peaks seen at the Jug Bay site broadened as they moved downstream due to advection and dispersion.

Table 4. Comparison of range in dissolved-phase herbicide concentrations from current and previous studies in the Patuxent River.†

Compound	1994‡	1995§	1996 (this study)
	μg/L		
Acetochlor	NA¶	<0.000035–0.12	<0.023–0.060
Alachlor	<0.000008–0.047	<0.000040–0.14	<0.023–0.540
Atrazine	0.016–0.026	0.0073–3.1	<0.023–1.29
CIAT#	NA	<0.000040–0.8	<0.023–0.76
Cyanazine	NA	<0.000050	<0.023
Metolachlor	<0.000006–0.0085	<0.00003–0.07	<0.023–0.61
Simazine	0.011–0.068	<0.000050–2.7	<0.023–0.049

† The values in the concentration range indicated as "<" represent the analytical detection limit of the method.
‡ Samples in this study collected only from Solomons station (10-L sample volume) (data from Harman-Fetcho et al., 1999).
§ Samples collected from Jug Bay, Benedict Bridge, and Solomons (2-L sample volume) (data from Harman-Fetcho et al., 1999).
¶ Not analyzed in this study.
# Triazine degradation product (6-amino-2-chloro-4-isopropylamino-*s*-triazine).

The effect of physical transport on upstream herbicide inputs can be examined by plotting concentrations measured in the three estuary transects (15 April, 10 May, and 22 May) versus salinity (Fig. 4). On 15 April, just before corn planting, only metolachlor and atrazine were detected and only at the upstream locations, with a severe drop-off in concentration at salinity greater than approximately 3. This may indicate that a pulse of herbicide-laden water was beginning to move down river. Results from the 10 May cruise, one day after a rain event, are more difficult to interpret. The three uppermost stations all had zero salinity, but concentrations of all the herbicides were highest at the Upper Marlboro site, not Jug Bay (Fig. 1). This may indicate the presence of a source of herbicides entering the estuary below Jug Bay, or, alternatively, the movement of a pulse that originated upstream. Results from the 22 May cruise also show the highest concentrations at the lowest salinity stations with a more gradual decline with salinity to the mouth of the river. These results also indicate that herbicides that entered the estuary in early May had begun to reach the lower reaches of the estuary by 22 May.

Adams and Thurman (1991) and others (Kolpin et al., 1995) have found that degradation of atrazine and other triazines occurs in soil and the degradation products CIAT and CEAT are frequently found in shallow aquifers in corn-producing regions of the USA. Studies of the microbial degradation of atrazine in soil indicate that the rate of formation of CIAT is approximately twice that of CEAT (Shelton et al., 1995). The chemical structure of simazine requires that only CEAT may be formed through dealkylation reactions (Fig. 2). The ratio of CIAT to atrazine concentrations has been used by researchers (Adams and Thurman, 1991; Schottler et al., 1994; Thurman et al., 1991) to assess ground water contributions in river systems of the Midwestern USA where a value of >1 indicates a ground water source and values of <1 indicate runoff of the parent atrazine. During the preplanting period from 4 April to 4 May, the median CIAT to atrazine ratio at Jug Bay was 3.41, suggesting a ground water source of the degradation products with little parent atrazine entering the system. After 5 May through the end of the study, the median ratio value was 0.62, indicating that runoff of the parent atrazine is contributing to the herbicide load in the river.

At the downstream stations, maximum concentra-

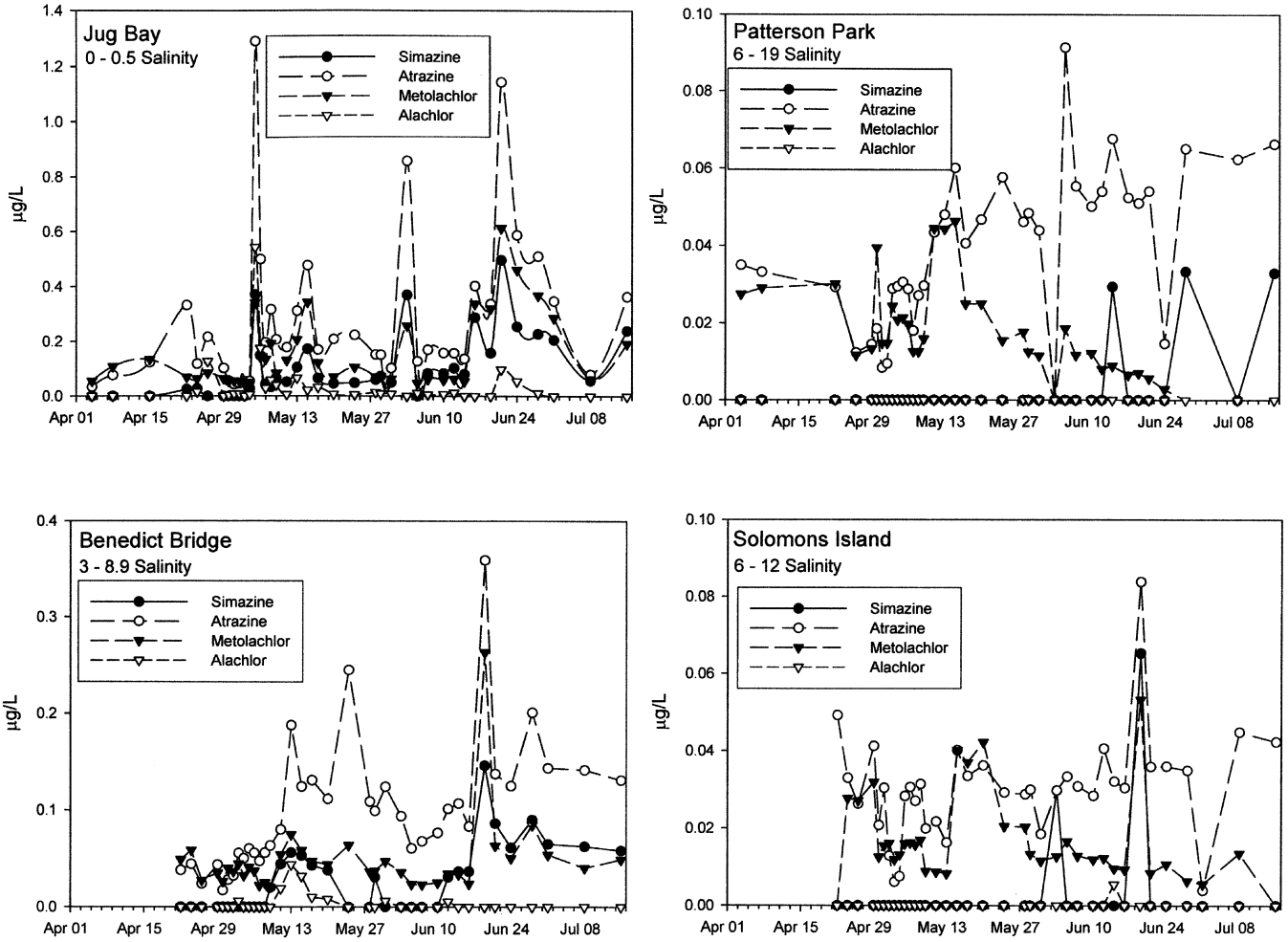

Fig. 3. Herbicide concentrations (µg/L) at the four collection sites.

tions of CEAT and CIAT increased relative to the parents, but detections of the breakdown products were much less consistent than the parent. CIAT was only detected in 3% of samples at Patterson Park and Solomons, while sharp, intense pulses of CEAT almost 10 times the concentration of atrazine were observed at the downstream sites from the end of April through May and early June. Since CEAT is the primary degradation product of simazine, this may indicate some local usage of simazine in the lower watershed. The infrequent nature of CEAT detections suggests that the chemical is episodically entering the estuary in the lower river region instead of continuously moving in from upstream locations or being generated by in situ degradation of triazines.

McFarland (1996) published a detailed study on the effects of agricultural practices on nitrate loads to ground water and surface waters of the Patuxent River watershed. The coastal plain site included in the McFarland study was very close to the Patterson Park site in our project. An in-depth description of the hydrogeologic structure of the site includes a 9.1-m-thick layer of quartz sand overlying a layer of low-permeability clay. The water table was found to slope toward the Patuxent River and follow the surface of the clay layer. Unconfined ground water was also present in the sand layer flowing toward the Patuxent River where it discharges. Discharge from the unconfined ground water may be the source of intermittent pulses of triazine degradation products in the lower estuary.

The upstream portion of the Patuxent River is generally shallow and slow moving with large wetland areas and high sediment loads (6.8–200 mg/L total suspended solids [TSS]), while the downstream areas are deep and wide with fast moving currents and lower sediment loads (3.0–19 mg/L TSS) (Table 1). Contaminated water will come in contact with sediment in the upper estuary to a much greater degree than the lower estuary. Ro and Chung (1995) conducted laboratory experiments examining the degradation of atrazine in slurry reactors of wetland sediment previously exposed to atrazine residues using wetland water under aerobic conditions. These conditions resulted in complete degradation of atrazine and its breakdown products in three weeks (CIAT, CEAT, and hydroxyatrazine were monitored). Repeated spiking of the sediment material with atrazine revealed that the sediment contained organisms that could efficiently degrade atrazine. However, the same group of scientists (Chung et al., 1995) found that with the same sediment under anaerobic conditions, atrazine

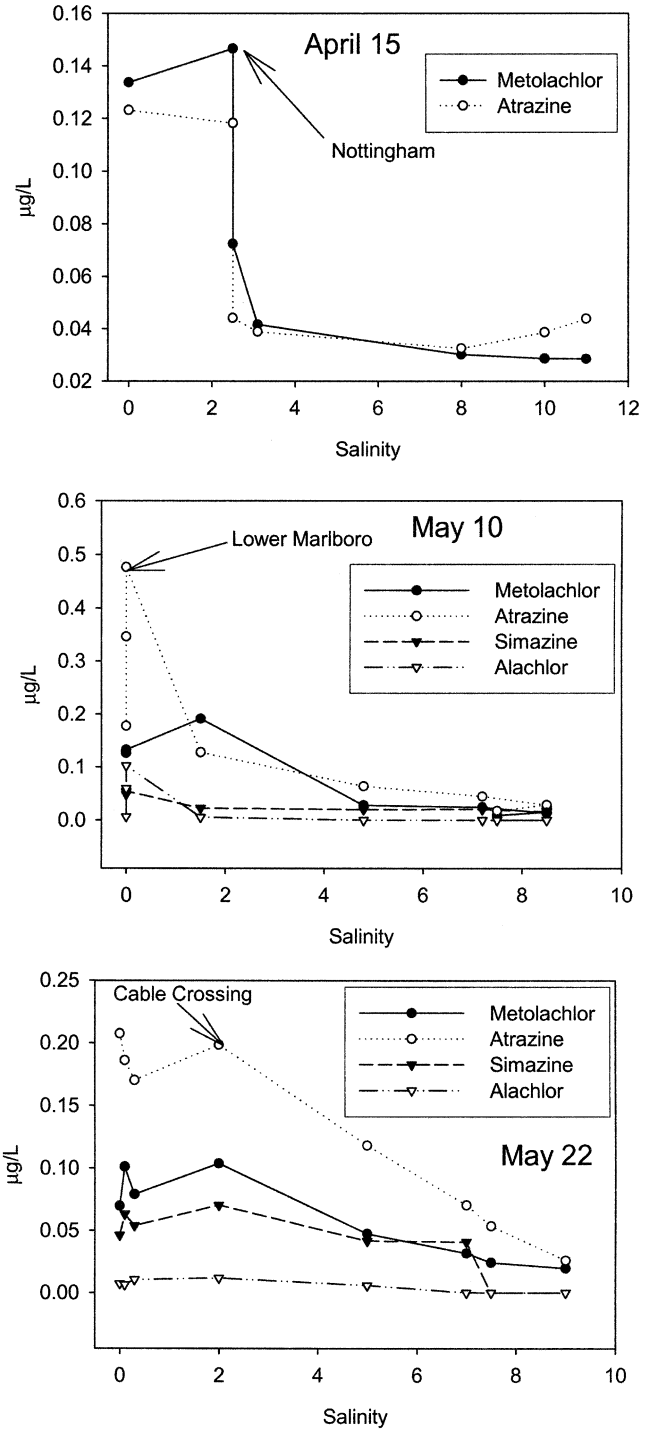

Fig. 4. Salinity mixing curves for atrazine concentration (µg/L) during the three transect cruises of the Patuxent River.

was much more persistent, with only 50% loss after 38 weeks and no formation of CIAT or CEAT. The only degradation product was hydroxyatrazine. From these studies we can infer that the upper estuary may be a zone of enhanced herbicide degradation as compared with the lower estuary, and microbial degradation of atrazine in open, flowing surface waters is not expected to be an important source of CEAT and CIAT.

Photolysis of atrazine to CIAT and CEAT could also occur in the water column. Indirect photolysis of atrazine via nitrate-mediated hydroxy radical processes has been observed in laboratory studies (Torrents et al., 1997), occurring much more quickly than direct photolysis. However, the presence of dissolved organic carbon in the water column was found to slow indirect photolysis processes significantly. Since photolysis can only occur during the day and since light will only penetrate the first few meters of water column, we may assume that formation of CIAT and CEAT from photolytic processes is probably not a significant source to the river.

Initial analysis of these results suggest that the presence of CEAT and CIAT is due to ground water discharge, and that these chemicals may be quickly degraded especially in shallow turbid waters. Atrazine appears to enter the estuary consistently from upstream locations due to runoff. Declining concentrations downstream indicate dilution combined with slow degradation, due to microbial or abiotic degradation. Further analysis of this data using the water transport model provides additional information about the sources, residence time, and environmental half-life of atrazine in the estuary.

Simulation Model Analysis of Atrazine Fate

Physical Transport Regime

Rainfall was above average throughout the Chesapeake Bay watershed in 1996, leading to above average river flow for both the Patuxent River and the other major Chesapeake Bay tributaries. Notably, Patuxent River flow did not decline from spring into summer, as regular rainfall during the study period maintained river flow. Freshwater inflow to the estuary, averaged over rolling 1-mo periods varied narrowly, between 26 and 29 m^3/s.

Physical transport rates in Patuxent estuary were not correlated with freshwater inflow during 1996, consistent with the findings of Hagy et al. (2000). Rather, advective exchange with Chesapeake Bay increased during early May and declined through June. These effects extended up the estuary, increasing transport within the estuary approximately twofold during May. Daily estimates of physical transport rates were used to simulate transport of pesticides in the estuary, using measured values at the landward and seaward ends of the estuary (Jug Bay and Chesapeake Biological Laboratory) as boundary conditions.

Conservative vs. Nonconservative Transport of Atrazine

Simulations were used to evaluate several alternative scenarios for transport and degradation of atrazine in the estuary. Each scenario involved different assumptions about atrazine decay rates and local inputs of atrazine to the estuary portion of the river. Although these simulations cannot provide a precise estimate of the atrazine half-life ($t_{1/2}$), they can suggest which combinations of rates are most consistent with the field observations. In the base scenario, it was assumed that atrazine

was transported conservatively through the estuary (i.e., $t_{1/2} = \infty$). Mixing diagrams have been used to examine transport of dissolved substances in estuaries (e.g., Fisher et al., 1998); however, significant end-member variability on short time scales, as was observed in this study, can complicate interpretation of anomalies in mixing diagrams (e.g., Fig. 4; Loder and Reichart, 1981; Cifuentes et al., 1990). Dynamic simulations overcome this problem with mixing diagrams and successfully described the general pattern of concentrations within the estuary and over time (Fig. 5). The simulations also reproduced the generally lower variability in atrazine concentrations that was observed at down-estuary sites as compared with Jug Bay. However, simulations assuming conservative mixing of atrazine predicted summer average concentrations exceeding observed values by nearly 50% in the upper estuary and 25% in the lower estuary (Table 5). These results suggested that atrazine degraded during transport through the estuary.

Scenarios that provided for first-order decay of atrazine could be calibrated to predict the summer average atrazine concentrations (Table 5). However, simulations using a single half-life for the entire estuary could not be calibrated to simultaneously predict concentrations at both Benedict Bridge and Patterson Park (Table 5). When these simulations correctly predicted concentrations at Benedict Bridge ($t_{1/2}$ = 21 d, no local inputs), estimated concentrations for Patterson Park were 32% lower than observed values. Conversely, when simulations correctly predicted concentrations at Patterson Park ($t_{1/2}$ = 67 d, no local inputs), concentrations at Benedict Bridge were overestimated by 30%. These results suggest that atrazine degraded much faster in the upper estuary than in the lower estuary, consistent with expectations based on laboratory degradation studies (Rice et al., 1997).

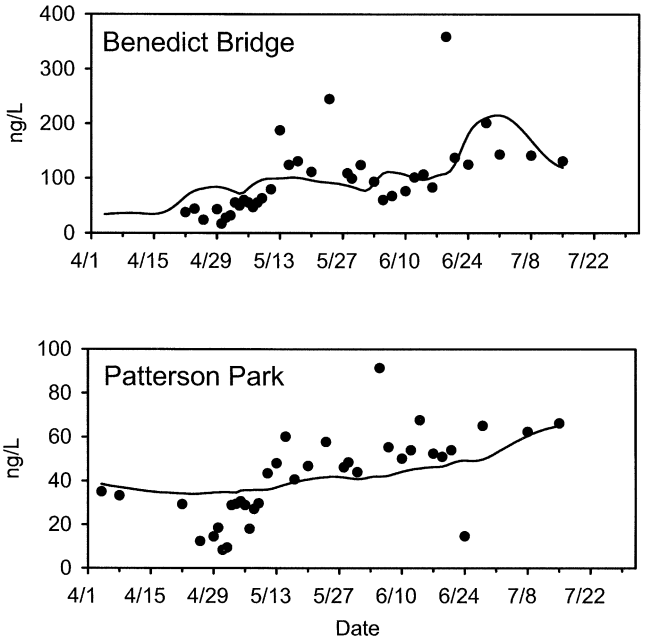

Fig. 5. Time series of observed and simulated atrazine concentration at the Benedict Bridge and Patterson Park locations during 1996. Model results are from the final scenario in which the half-life for atrazine in the upper and lower estuary was set to $t_{1/2}$ = 20 d (upper estuary) and $t_{1/2}$ = 100 d (lower estuary). This resulted in identical mean values for observed and simulated concentrations at both sites.

Model simulations that provided for different atrazine decay rates in the upper and lower estuary could be calibrated to correctly predict the average concentration at both sites ($t_{1/2}$ = 20 d for the upper estuary, $t_{1/2}$ = 300 d for the lower estuary). However, the $t_{1/2}$ = 300 d for the lower estuary is improbably long as it exceeds laboratory estimates for sterile seawater by a substantial margin (Rice et al., 1997). An alternative explanation is that freshwater entering the lower estuary carried an additional input of pesticides to the estuary, consistent with the presence of some agricultural land uses in the lower watershed. Local herbicide inputs were modeled by assuming that the concentration of atrazine in freshwater entering the lower estuary was proportional to concentrations observed at Jug Bay, reflecting the probability that pesticide application and rainfall events occurred within similar time periods in both the upper and lower watershed. As an initial estimate, it was assumed that freshwater inputs entering the lower estuary had the same atrazine concentration as was observed at Jug Bay. Model calibration revealed that under this scenario, the estimated half-life for atrazine in the lower estuary was 100 d (Table 5), a reasonable estimate given available laboratory estimates. While this argument might be logically extended to suggest that the half-life of atrazine was the same in the lower estuary as in the upper estuary, such a scenario would require that lower estuary freshwater inputs bear atrazine concentrations approximately sevenfold greater than observations at Jug Bay, an unlikely possibility. While the simulation models cannot provide certain descriptions of the degradation and transport of atrazine in the estuary, they suggest that: (i) atrazine decays in the estuarine environment, (ii) atrazine decays much more slowly in the open water environment of the lower estuary than in the upper estuary, and (iii) atrazine enters the lower estuary not only from upstream sources, but from freshwater inputs entering the estuarine portion of the river.

Atrazine Mass Balance

A mass balance for atrazine was assembled for Patuxent River for the period 4 Apr. 1996 to 15 July 1996.

Table 5. Comparison of observed mean atrazine concentrations at the Benedict Bridge and Patterson Park locations with corresponding averages resulting from simulations under each of five scenarios.

Scenario	Benedict Bridge	Patterson Park
	µg/L	
Observed†	0.103	0.044
Conservative transport	0.153	0.055
$t_{1/2}$ = 21 d (no local inputs)	0.103	0.030
$t_{1/2}$ = 67 d (no local inputs)	0.134	0.045
$t_{1/2}$ = 20 d (upper), 300 d (lower)	0.104	0.044
$t_{1/2}$ = 20 d (upper), 100 d (lower), + local inputs	0.103	0.043

† Mean of estimated daily concentrations interpolated from raw observations using a cubic spline.

During that period (103 d), 66 kg of atrazine was estimated to have entered the estuary from the river and an additional 5 kg entered the estuary directly from freshwater sources in the lower watershed. Of the riverine inputs, 38 kg (58%) was transported from the upper estuary to the lower estuary. Export to Chesapeake Bay amounted to 21 kg or 31% of total inputs (Fig. 6). Estimated internal losses amounted to 23 and 11 kg in the upper and lower estuary, respectively, for a total of 34 kg (48%). The remaining 15 kg was estimated to have accumulated in the estuary, as reflected in the increasing concentrations.

The fraction of atrazine transported down-estuary and ultimately exported to Chesapeake Bay may have been greater in 1996 than in an average year due to the effect of high river flow on water residence time. At the average river flow rate of 26 to 29 m^3/s during the 1996 study period, flow averaged 25 to 100% greater than in the average year. Consequently, freshwater transits the upper estuary (volume = 50.8×10^6 m^3) in approximately 20 d (approximately equal to freshwater fill time). This explains why nearly 60% of the atrazine input was transported down-estuary, despite the short half-life of atrazine in the upper estuary. In an average year, longer water residence times in the upper estuary, approximately 30 d, would tend to decrease the amount transported seaward to approximately 50% and increase the amount degraded. Because the estimated half-life of atrazine in the lower estuary ($t_{1/2}$ = 100 d) is much longer than in the upper estuary ($t_{1/2}$ = 20 d), the effect of river flow on the residence time of atrazine in the upper estuary has an important effect on the overall fate of the pesticide.

The residence time of water in the lower estuary is approximately 25 d and varies much less with Patuxent River flow than does residence time for the upper estuary. Instead, flushing of the lower estuary tends to reflect salinity distributions and weather-related factors that drive the gravitational circulation of the lower estuary (Hagy et al., 2000). Thus, the effect of river flow on the fate of atrazine once it reaches the lower estuary is less clear than for the upper estuary. Given $t_{1/2}$ = 100 d for atrazine in the lower estuary and residence time T = 25 d, only 15% of the atrazine reaching the lower estuary would be expected to decay before being exchanged with Chesapeake Bay water. However, the net transport of atrazine from Patuxent River estuary to Chesapeake Bay depends on the gradient of atrazine concentration across the estuary mouth, whereas increased atrazine concentrations in Chesapeake Bay relative to Patuxent River decrease the flux of atrazine into to the bay. In the extreme case where atrazine is not present in Chesapeake Bay, one can expect that 85% of the atrazine reaching the lower Patuxent River will be flushed into the bay. More realistically, a smaller fraction is transported seaward and more than 15% of atrazine inputs to the lower Patuxent are degraded. For example, this study estimated that only 50% of inputs to the lower estuary were flushed to Chesapeake Bay (Fig. 6). If atrazine concentrations in the bay exceeded Patuxent River concentrations, the net pesticide flux would be directed landward, generating additional loading to Patuxent River. Thus, in attempting to predict the fate of a pesticide in an estuarine environment, it is important to know the concentrations at the boundaries of the study area, in this case, Chesapeake Bay.

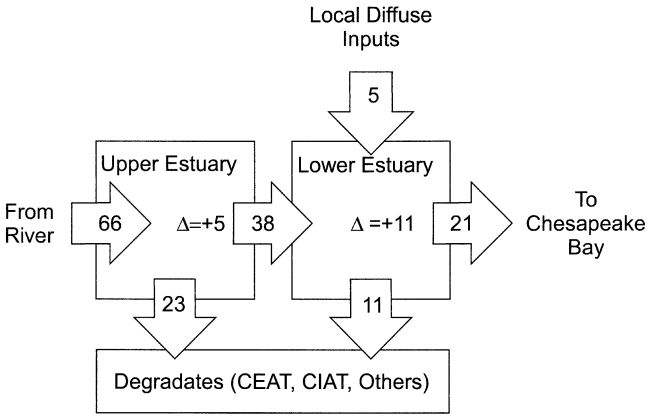

Fig. 6. A mass balance for atrazine in the upper and lower Patuxent River estuary during 6 Apr. to 15 July 1996 computed from the final simulation scenario (i.e., assuming $t_{1/2}$ = 20 d for the upper estuary and $t_{1/2}$ = 100 d for the lower estuary, and permitting diffuse inputs to the lower estuary). Arrows depict transport (inflow from Patuxent River, inflow from diffuse local sources to the lower estuary, transport from upper estuary to lower estuary, net export to Chesapeake Bay), degradation (upper and lower estuary), and accumulation in the estuary. All units are kilograms.

CONCLUSIONS

While results of this study are limited to only one growing season in one estuary of the larger Chesapeake Bay system, some important conclusions can be made regarding the fate of common herbicides in estuaries of the Mid-Atlantic region where agricultural practices are similar. First, atrazine is most efficiently transported to surface waters and it is the most persistent herbicide compared with metolachlor, alachlor, acetochlor, simazine, cyanazine, and pendamethalin. Second, in modeling herbicide fate in an estuary, the surface water half-life value should be adjusted depending on the nature of different sections of the estuary. Shallow surface waters with high sediment content may provide an opportunity for microbial degradation and photolysis (for those photosensitive chemicals) to occur more rapidly than in deeper, less turbid estuaries. These results also indicate that once atrazine or other herbicide residues enter the open waters of the Chesapeake Bay, they are likely to be quite persistent. The main stem Chesapeake Bay water may sometimes be a source of herbicides to its tributaries. These results support the idea of protecting shallow wetland areas in agricultural regions and the use of constructed wetland areas as "reactors" for treating agricultural runoff waters before they are released to creeks and rivers.

REFERENCES

Adams, C.D., and E.M. Thurman. 1991. Formation and transport of deethylatrazine in the soil and vadose zone. J. Environ. Qual. 20: 540–547.

Aga, D.S., and E.M. Thurman. 2001. Formation and transport of the sulfonic acid metabolites of alachlor and metolachlor in soil. Environ. Sci. Technol. 35:2455–2460.

Chung, K.H., K.S. Ro, and D. Roy. 1995. Atrazine biotransformation in wetland sediment under different nutrient conditions I: Anaerobic. J. Environ. Sci. Health. Part A Environ. Sci. Eng. Toxic Hazard. Subst. Control A30:109–120.

Cifuentes, L.A., L.E. Schemel, and J.H. Sharp. 1990. Qualitative and numerical analyses of the effects of river inflow variation on mixing diagrams in estuaries. Estuarine Coastal Shelf Sci. 30:411–427.

DeLorenzo, M.E., G.I. Scott, and P.E. Ross. 1999. Effects of the agricultural pesticides atrazine, deethylatrazine, endosulfan, and chlorpyrifos on an estuarine microbial food web. Environ. Toxicol. Chem. 18:2824–2835.

Detenbeck, N.E., R. Hermanutz, K. Allen, and M.C. Swift. 1996. Fate and effects of the herbicide atrazine in flow-through wetland mesocosms. Environ. Toxicol. Chem. 15:937–946.

Fairchild, J.F., D.S. Ruessler, and A.R. Carlson. 1998. Comparative sensitivity of five species of macrophytes and six species of algae to atrazine, metribuzin, alachlor and metolachlor. Environ. Toxicol. Chem. 17:1830–1834.

Fisher, T.R., J.D. Hagy, and E. Rochelle-Newall. 1998. Dissolved and particulate organic carbon in Chesapeake Bay. Estuaries 21:215–229.

Foster, G.D., and K.A. Lippa. 1996. Fluvial loadings of selected organonitrogen and organophosphorus pesticides to Chesapeake Bay. J. Agric. Food Chem. 44:2447–2454.

Foster, G.D., K.A. Lippa, and C.V. Miller. 2000. Seasonal concentration of organic contaminants at the fall line of the Susquehanna River Basin and estimated fluxes to northern Chesapeake Bay, USA. Environ. Toxicol. Chem. 19:992–1001.

Glotfelty, D.E., A.W. Taylor, A.R. Isensee, J. Jersey, and S. Glenn. 1984. Atrazine and simazine movement to Wye River estuary. J. Environ. Qual. 13:115–121.

Godfrey, J.T., G.D. Foster, and K.A. Lippa. 1995. Estimated annual loads of selected organic contaminants to Chesapeake Bay via a major tributary. Environ. Sci. Technol. 29:2059–2064.

Graham, W.H., D.W. Graham, F. Denoyelles, V.H. Smith, C.K. Larive, and E.M. Thurman. 1999. Metolachlor and alachlor breakdown product formation patterns in aquatic field mesocosms. Environ. Sci. Technol. 33:4471–4476.

Hagy, J.D., L.P. Sanford, and W.R. Boynton. 2000. Estimation of net physical transport and hydraulic residence times for a coastal plain estuary using box models. Estuaries 23:328–340.

Harman-Fetcho, J.A., L.L. McConnell, and J.E. Baker. 1999. Agricultural pesticides in the Patuxent River, a tributary of the Chesapeake Bay. J. Environ. Qual. 28:928–938.

Jeffers, J.N.R. 1988. SCOPE 34: Practitioner's handbook on the modelling of dynamic change in ecosystems. Sci. Committee on Problems of the Environ., John Wiley & Sons, New York.

Jin-Clark, Y., M.J. Lydy, and K.Y. Zhu. 2002. Effects of atrazine and cyanazine on chlorpyrifos toxicity in *Chronomus tentans* (Diptera: Chironomidae). Environ. Toxicol. Chem. 21:598–603.

Kolpin, D.W., D.A. Goolsby, and E.M. Thurman. 1995. Pesticides in near-surface aquifers: An assessment using highly sensitive analytical methods and tritium. J. Environ. Qual. 24:1125–1132.

Lehotay, S.J., J.A. Harman-Fetcho, and L.L. McConnell. 1999. Agricultural pesticide residues in oysters and water from two Chesapeake Bay tributaries. Mar. Pollut. Bull. 37:32–44.

Linker, L.C., G.W. Shenk, R.L. Dennis, and J.L. Sweeney. 1999. Cross-media models for the Chesapeake Bay watershed and airshed. Chesapeake Bay Program, Annapolis, MD.

Liu, B., L.L. McConnell, and A. Torrents. 2002. Herbicide and insecticide loading from the Susquehanna River to the northern Chesapeake Bay. J. Agric. Food Chem. 50:4385–4392.

Loder, T.C., and R.P. Reichart. 1981. The dynamics of conservative mixing in estuaries. Estuaries 4:64–69.

Lytle, J.S., and T.F. Lytle. 1998. Atrazine effects on estuarine macrophytes *Spartina alterniflora* and *Juncus roemerianus.* Environ. Toxicol. Chem. 17:1972–1978.

Maryland Department of Agriculture. 1999. Maryland pesticide statistics for 1997. MDA-265-99. Maryland Dep. of Agric., Annapolis.

McFarland, E. R. 1996. Ground-water flow, geochemistry, and effects of agricultural practices on nitrogen transport at study sties in the Piedmont and Coastal Plain physiographic provinces, Patuxent River basin, Maryland. Open-File Rep. 94-507. U.S. Geol. Survey, Reston, VA.

Meister, R.T. (ed.) 2001. Farm chemicals handbook. Meister Publ., Willoughby, OH.

Montgomery, J.H. 1993. Agrochemicals desk reference: Enviornmental data. Lewis Publ., Chelsea, MI.

National Oceanic and Atmospheric Administration. 1996. Climatological data annual summary. Maryland and Delaware. Natl. Oceanic and Atmospheric Admin., Natl. Climatic Data Center, Asheville, NC.

Officer, C.B. 1980. Box models revisited. *In* P. Hamilton and R.B. Macdonald (ed.) Estuarine and wetland processes. Marine Sciences Series. Vol. 11. Plenum Press, New York.

Pape-Lindstrom, P.A., and M.J. Lydy. 1997. Synergistic toxicity of atrazine and organophosphate insecticides contravenes the response addition mixture model. Environ. Toxicol. Chem. 16:2415–2420.

Pennington, P.L., and G.I. Scott. 2001. Toxicity of atrazine to the estuarine phytoplankter *Pavlova* sp. (prymnesiophyceae): Increased sensitivity after long-term, low-level population exposure. Environ. Toxicol. Chem. 20:2237–2242.

Pritchard, D.W. 1952. Salinity distribution and circulation in the Chesapeake estuarine system. J. Mar. Res. 11:106–123.

Pritchard, D.W. 1969. Dispersion and flushing of pollutants in estuaries. J. Hydraul. Div. Am. Soc. Civil Eng. 95:115–124.

Rice, P.J., T.A. Anderson, and J.R. Coats. 1997. Phytoremediation of herbicide-contaminated surface water with aquatic plants. p. 54–65. *In* E.L. Kurger et al. (ed.) Phytoremediation of soil and water contaminants. ACS Symp. Ser. 664. Am. Chem. Soc., Washington, DC.

Ro, K.S., and K.H. Chung. 1995. Atrazine biotransformation in wetland sediment under different nutrient conditions II: Aerobic. J. Environ. Sci. Health. Part A Environ. Sci. Eng. Toxic Hazard. Subst. Control A30:121–131.

SAS Institute. 1993. SAS/ETS user's guide. Version 6. 2nd ed. SAS Inst., Cary, NC.

Schottler, S.P., S.J. Eisenreich, and P.D. Capel. 1994. Atrazine, alachlor, and cyanazine in a large agricultural river system. Environ. Sci. Technol. 28:1079–1089.

Shelton, D.R., A.M. Sadeghi, J. Karns, and C.J. Hapeman. 1995. Effect of wetting and drying of soil on sorption and biodegradation of atrazine. Weed Sci. 43:298–305.

Thurman, E.M., D.A. Goolsby, M.T. Meyer, and D.W. Kolpin. 1991. Herbicides in surface waters of the Midwestern United States: The effect of spring flush. Environ. Sci. Technol. 25:1794–1796.

Torrents, A., B. Anderson, S. Bilboulian, W.E. Johnson, and C.J. Hapeman. 1997. Atrazine photolysis: Mechanistic investigations of direct and nitrate mediated hydroxy radical processes and the influence of dissolved organic carbon from the Chesapeake Bay. Environ. Sci. Technol. 31:1476–1482.

USEPA. 1983. Standard methods for the examination of water and wastewater under total organic carbon. USEPA methods for chemical analysis of water. EPA-600/4-7-020. USEPA, Cincinnati, OH.

USEPA. 2002. Chesapeake Bay water quality monitoring program data [Online]. Available at http://www.chesapeakebay.net/data/index.htm (verified 11 Nov. 2003). USEPA Chesapeake Bay Program Office, Annapolis, MD.